



Synergetic effect of a pillared bentonite support on Se(VI) removal by nanoscale zero valent iron



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ABSTRACT

A positively-charged pillared bentonite (Al-bent) was used as the carrier of nanoscale zerovalent iron (NZVI) particles for accelerating the reductive removal of anionic Se(VI) from water by NZVI. A synergetic effect on Se(VI) removal by this NZVI/Al-bent composite was observed, with removal efficiency (95.7%) much higher than the sum (72.0%) of NZVI reduction (62.1%) and Al-bent adsorption (9.86%). The multiple roles of Al-bent in the reaction system of Se(VI) with NZVI were comprehensively investigated using XAFS techniques, XRD analysis, kinetic studies and pH monitoring. The results indicate that the positively-charged Al-bent as a good adsorbent to anionic Se(VI) accelerated the reductive transformation of Se(VI) into less soluble Se(-II). Al-bent also acted as a pH buffering agent, and contributed to the enhanced stability and reusability of NZVI. In addition, Al-bent could transfer the insoluble reduction products away from the iron surface according to EXAFS studies. Particularly, Al-bent could activate Fe(II) ions generated in the reaction system through an appropriate bonding at pH 8.0, and provide NZVI with an extra reduction capacity. The results indicate the significance of correct matching of bentonite support to target contaminant for developing novel remediation technique based on this natural mineral.

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1. Introduction

Groundwater contamination by selenium (Se) compounds has become a significant environmental problem due to the increasing anthropogenic activities, such as mining operations, combustion of coal and other fossil fuels, and agricultural irrigation with Se-containing water [1–3]. In addition, nuclear industry can also produce a certain amount of radioactive Se [4,5]. The species and toxicity of Se in the natural environment are dependent on geochemical conditions. Under aerobic conditions, the main forms of Se are soluble oxyanions including selenate (SeO_4^{2-} or Se(VI)) and selenite (SeO_3^{2-} or Se(IV)). Se(VI) is the most oxidized form with high solubility in water, and generally considered to be the most toxic species. Se(IV) is less available to organisms because of its affinity to adsorption sites of sediment and soil constituents [6,7]. During the infiltration of surface water, the mobile Se(VI) is weakly adsorbed by minerals, and thus, becomes the main species in groundwater [1]. So, strategies for the removal of soluble Se in

water will most likely involve reduction of Se(VI) into Se species with lower valence (Se(0) or Se(-II)).

Among the various treatment technologies, application of zerovalent iron (ZVI) in Se(VI) and Se(IV) removal is preferred because of its low cost and toxicity, easy operation and no secondary pollution [1,8]. As the reduction of contaminants by iron is surface mediated, thus nanoscale zerovalent iron (NZVI) has received more attention since it provides larger surface area and higher reactivity [9–14]. For example, Olegario et al. [5] found that the removal of Se(VI) by NZVI was much higher than that by micrometer iron. However, NZVI particles are unstable and tend to agglomerate because of their high surface energies and intrinsic magnetic interactions, leading to the restrained chemical reactivity [15–17]. To overcome this drawback, the use of mechanical supports such as PVA microspheres [18], resins [19], multiwalled carbon nanotubes [20], cationic exchange membrane [21], porous carbon [22,23] and silica [24,25] to immobilize NZVI has been tested.

Different from those synthetic mechanical supports, bentonite is a kind of layered clay composed mainly of montmorillonite, which is an important constituent of soils and a natural adsorbent to many kinds of contaminants including Se [26]. So, investigations on the role of bentonite in removal of contaminants by ZVI

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are of particular significance on accelerating the degradation of contaminants in natural environment [27]. For instance, Chen and co-workers used bentonite as the support of NZVI, and found that the bentonite-supported NZVI showed higher removal efficiency to both metal ions (Cr(VI)) [28] and organic contaminants (methyl orange and acid violet red B) [29,30], in comparison to the bare NZVI. Furthermore, bentonite can be easily modified by intercalating various functional groups into interlayers, so as to achieve better adsorption property to target contaminants and to optimize its advantages as the support of NZVI. For example, the enhanced removal of organic contaminants by NZVI supported on organobentonite [16] and the accelerated reduction of cationic UO_2^{2+} by NZVI supported on negatively-charged bentonite (Na-bent) have been reported in our previous research [31]. However, the mechanisms for such enhanced removal are still worthy of further investigation, and the roles of bentonite need to be fully discovered, so as to introduce the bentonite-supported NZVI for remediation of other more environmental contaminants.

In present work, the removal of anionic SeO_4^{2-} (Se(VI)) in water by NZVI supported on a positively-charged pillared bentonite (Al-bent) was studied and compared with that by bare NZVI and Na-bent-supported NZVI. XAFS techniques, along with XRD analysis, kinetic studies and pH monitoring, were used to investigate the synergetic effect of bentonite-supported NZVI for the enhanced Se(VI) removal. The multiple functions of Al-bent (such as adsorption of Se(VI), pH buffering and transferring the insoluble reduction products) in the reaction system of Se(VI) with NZVI were comprehensively explored.

2. Materials and methods

2.1. Materials

The original bentonite (Na-bent) composed primarily of Na^+ -montmorillonite was purchased from Inner Mongolia, China; its cation exchange capacity (CEC) is determined to be 115 cmol/kg. Commercial iron powder (ZVI) was obtained from Shanghai Chemical, China, and the grain size passing through a sieve of 100 mesh (size < 150 μm) was selected and used without further treatment. All the other chemicals (including four Se reference compounds: Na_2SeO_4 , Na_2SeO_3 , Se, FeSe) were purchased in analytical purity and used without any further purification in our experiments. All the solutions were prepared with 18 M Ω cm (Milli-Q Gradient, Millipore, USA) deionized water under ambient conditions. NZVI sample and two bentonite-supported NZVIs (NZVI/Na-bent and NZVI/Al-bent) were prepared by a previously reported procedure [15], with details shown in Text S1 in supporting information (SI).

2.2. Batch experiments for Se(VI) removal

Typically, each of the four iron sources including ZVI (0.0329 g), NZVI (0.0565 g), NZVI/Al-bent (0.142 g) and NZVI/Na-bent (0.129 g) was added into 150 mL conical flask containing 100 mL of Se(VI) solution (initial pH = 6, and initial concentration $C_0 = 20$ mg/L, 0.01 mol/L NaCl, unless otherwise specified). In these treatments, the four iron sources were used at the same dose of iron, i.e., 0.300 g/L. Besides, Al-bent (0.112 g) and Na-bent (0.099 g) alone were also used in a separate treatment and the dosage was same as that used in the NZVI/Al-bent and NZVI/Na-bent treatment. The Se(VI) stock solution was deoxygenated by N_2 stream for 10 min before addition of iron sources, and kept sealed with stopper during the reaction. The removal experiment was carried out by putting the flask in a thermostatic shaker bath at $25 \pm 0.5^\circ\text{C}$ for 120 min, with a rotation speed of 150 rpm. At the given time interval, 1 mL of solution was sampled and filtered through a 0.22 μm membrane.

The Se(VI) concentrations at time t (C_t , mg/L) were determined, and the removal of Se(VI) was calculated according to the following equation, removal (%) = $(C_0 - C_t)/C_0 \times 100\%$. The data of batch experiments were obtained in triplicates. Besides, the adsorption isotherms of Se(VI) on Al-bent and Na-bent were measured, and detailed methods were shown in Text S2 in SI.

The stability and reusability of iron samples during Se(VI) removal was investigated by repetitive experiments as following: At pH = 6.0, 100 mL Se(VI) solution was mixed with a certain amount of NZVI and NZVI/Al-bent. After 120 min, 2 mL solution was sampled from the flask for analysis of Se(VI) concentration, and then an additional 2 mL Se(VI) solution with a proper concentration was added. For this purpose, Se(VI) concentration and pH remained the same at the beginning of each of the four cycles.

2.3. Analytical methods

Concentrations of Se(VI) in solution were analyzed by using Hydride generation atomic absorption spectrometry (HG-AAS, (AA-6300C, Shimadzu)). The solution pH was measured with a pH meter (PHS-2C, China). Zeta potential was measured by nano-ZS model (Malvern) zetasizer instrument. X-ray diffraction (XRD) measurement was performed with a Rigaku D/MAX-2500 system using Cu K α radiation at 0.1542 nm. Transmission electron microscope (TEM) images were obtained in a JEM-1010 instrument using an accelerating voltage of 80 kV. Se K-edge XAFS spectra at 12,684.5 eV were recorded at room temperature at Shanghai Synchrotron Radiation Facility (SSRF, China), and the details are presented in Text S3 in SI.

3. Results and discussion

3.1. Accelerated removal of Se(VI) by NZVI supported on the pillared bentonite

The removal efficiencies of Se(VI) by various iron sources are all presented in Fig. 1. It indicates that the removal efficiency of Se(VI) by ZVI was only 4.8% within 120 min. While a much higher removal efficiency (62.1%) was obtained in the NZVI treatment. The significant increase of removal efficiency of Se(VI) by NZVI is due to the smaller particle size (~ 100 nm) of NZVI than that of ZVI (~ 150 μm). The smaller size of iron particles is indicative of larger surface area that offers more reactive sites for Se(VI) reaction [32]. Furthermore, the removal efficiency of Se(VI) by NZVI/Al-bent was 95.7%, which was not only much higher than that by NZVI (62.1%), but also greater than the sum (72.0%) of reduction by NZVI plus

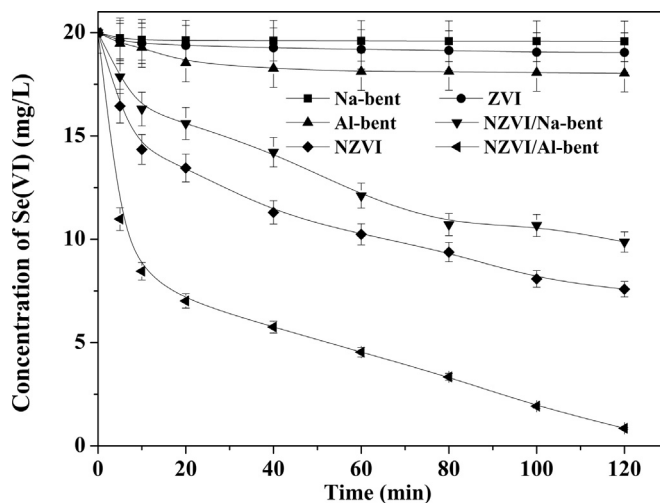
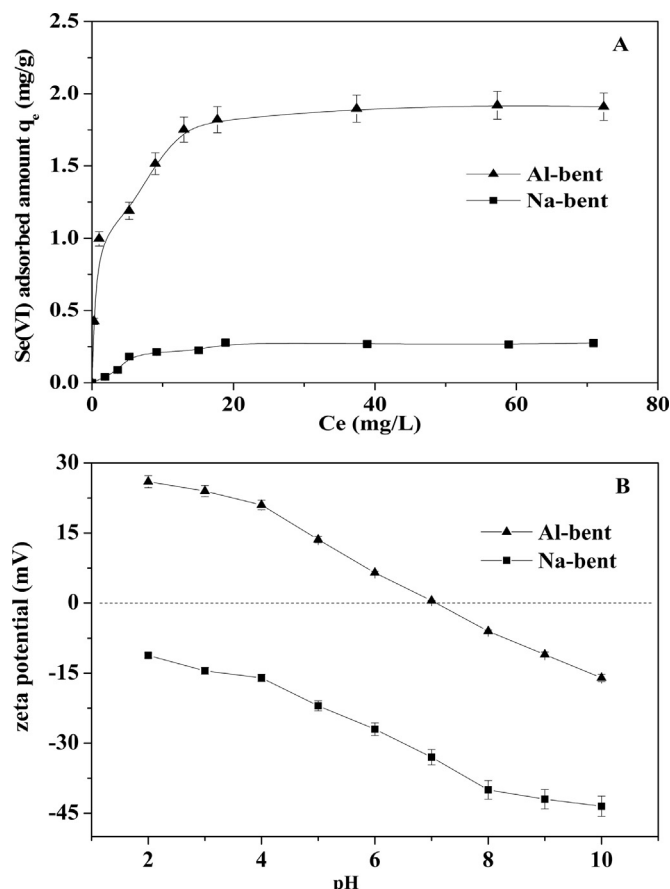


Fig. 1. Removal efficiencies of Se(VI) by four iron sources and two bentonites.

Table 1
Parameters for kinetics of Se(VI) reduction

Iron sample	Fitted equation	k_1 (mmol/(L · min))	k_2 (L/mmol)	R
NZVI	$\frac{1}{r_0} = 0.293 + 22.5 \frac{1}{C_0}$	3.42	0.0130	0.994
NZVI/Al-bent	$\frac{1}{r_0} = 0.207 + 8.37 \frac{1}{C_0}$	4.84	0.0294	0.999
NZVI/Na-bent	$\frac{1}{r_0} = 0.3343 + 29.019 \frac{1}{C_0}$	2.99	0.0115	0.941

**Fig. 2.** (A) Adsorption isotherms of Se(VI) on Na-bent and Al-bent, (B) Zeta potential of Na-bent and Al-bent as a function of solution pH.

adsorption (9.86%) by Al-bent. This indicates that synergetic effect on Se(VI) removal exists in the NZVI/Al-bent composite system.

The synergetic effect of Al-bent is firstly related to its higher adsorption capacity to Se(VI) than Na-bent, as indicated by the adsorption isotherms of Se(VI) on Na-bent and Al-bent, respectively (Fig. 2A). The higher adsorption of Se(VI) by Al-bent is related to its surface electrical property and functional groups. According to the zeta potentials of Na-bent and Al-bent determined at a pH range from 2.0 to 10.0 (Fig. 2B), a negatively-charged surface of Na-bent is indicated by the negative zeta potentials. However, the zeta potentials of Al-bent are positive at pH below pH_{PZC} (the pH_{PZC} of Al-bent is ~ 7.0), which is indicative of a positively-charged surface of Al-bent under our condition. So, the positively-charged Al-bent favors the adsorption of anionic Se(VI), and thus more Se(VI) can be enriched in the solid phase, making Se(VI) more easily reacted with NZVI. In summary, Al-bent facilitated the mass transfer of Se(VI) from solution to iron surface, leading to the acceleration of surface reaction. In contrast, the removal efficiency of Se(VI) by NZVI/Na-bent only reached 50.7%, lower than that by NZVI or NZVI/Al-bent. The reason may be related to the poor adsorption of Se(VI) by Na-bent.

Contribution of surface adsorption on the synergetic effect can be proved by kinetic studies of Se(VI) removal by NZVI, NZVI/Na-bent and NZVI/Al-bent. For this purpose, a series of removal experiments were carried out at various initial Se(VI) concentrations (20, 40, 60, 80 mg/L), with results showing in Fig. S1. Obviously, the removal efficiencies by NZVI/Al-bent were higher than either those by NZVI alone or those by NZVI/Na-bent at the same initial Se(VI) concentration. Langmuir–Hinshelwood (L-H) kinetic model (Eq.1) that has been commonly used to describe surface-catalyzed reactions [33] was employed here to investigate the kinetics of Se(VI) reduction by NZVI, NZVI/Na-bent and NZVI/Al-bent.

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$$\frac{1}{r_0} = \frac{1}{k_1 k_2} \cdot \frac{1}{C_0} + \frac{1}{k_1} \quad (1)$$

Where r_0 is the initial reaction rate, C_0 is the initial concentration of Se(VI), and k_1 , k_2 are the reaction rate constant and adsorption coefficient, respectively. The fitting results of our experimental data with L-H model are shown in Table 1. The correlation coefficients close to 1 ($R > 0.990$) indicate that Se(VI) removal by NZVI, NZVI/Na-bent and NZVI/Al-bent can be well fitted to the L-H model. Both reaction rate constant k_1 and adsorption coefficient k_2 for Se(VI) removal were in the order of NZVI/Al-bent > NZVI > NZVI/Na-bent, suggesting that the reaction rate is positively related to the adsorption.

The K-edge X-ray absorption near-edge structure (XANES) spectra were used to investigate the mechanisms related to the synergetic effect of Al-bent as the support on Se(VI) removal. For this purpose, XANES spectra of four Se reference compounds of different oxidation states and reacted samples of Se(VI) with NZVI or NZVI/Al-bent at different reaction time are shown in Fig. 3. The edge shape clearly varied between both experimental samples and reference compounds, thus showing various oxidation states of Se. Depending on the Se oxidation state, the XANES spectra varied in terms of edge position. The measured E_0 values for Se(VI), Se(IV), Se(0), and Se(-II) were 12,666.54, 12,662.07, 12,658.56 and 12,657.04 eV, respectively, which were in accordance with those observed in a previous study [14]. The differences reflected variations in the structural environment of Se. For the samples of Se(VI) removal by NZVI/Al-bent at the three reaction time (10, 60, and 120 min), the XANES spectra are quite similar to that of Se(-II), suggesting that Se(VI) was completely reduced to Se(-II) under our experimental conditions. Nevertheless, for the samples of Se(VI) removal by NZVI after 60 min, the XANES spectra seem to be combined with that of Se(VI) and Se(-II), demonstrating that Se(VI) is not fully reduced by NZVI alone, with some of Se(VI) adsorbed on the solid. This result is in agreement with that reported by Yoon et al. [14], who found that Se(VI) could not be completely reduced to Se(-II) by ZVI. Besides, the XANES spectrum of the sample of Se(VI) removal by NZVI at a short reaction time (10 min) are more similar to the spectrum of Se(VI) than that at a long reaction time (e.g. 120 min), indicating that adsorbed Se(VI) can be reduced further to Se(-II) at a slow reaction rate. Therefore, the XANES analysis confirmed that using Al-bent as the support, the removal efficiency

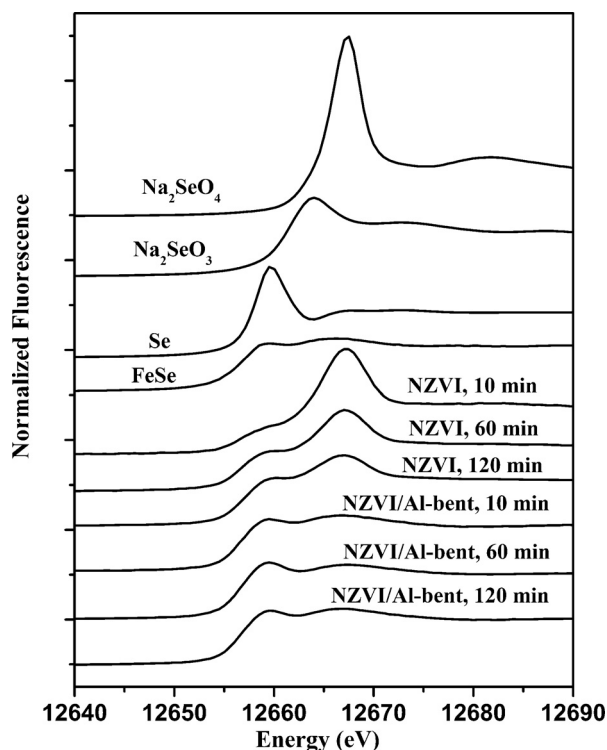


Fig. 3. X-ray absorption near-edge structure (XANES) spectra of four Se reference compounds of different oxidation states and two reacted samples with Se(VI).

of Se(VI) by NZVI are enhanced by accelerating the reductive transformation of Se(VI) into less soluble Se(-II) with low toxicity.

3.2. Enhanced stability and reusability of NZVI/Al-bent composite

Reusability of the different forms of NZVI is an important concern for their practical application. According to the recycling experiments of Se(VI) removal by NZVI and NZVI/Al-bent (Fig. 4), we found that the removal of Se(VI) by the bare NZVI decreased from 75.4% to 66.8% after four cycles, while the removal of Se(VI) only decreased from 99.2% to 95.5% in the NZVI/Al-bent treatment. The results indicate that Al-bent-supported NZVI displayed much higher stability and reusability, in addition to the above-mentioned higher reactivity than the bare NZVI. The reason for such enhancement is partly related to the well dispersion of NZVI particles in the bentonite carrier, as that observed by transmission electron

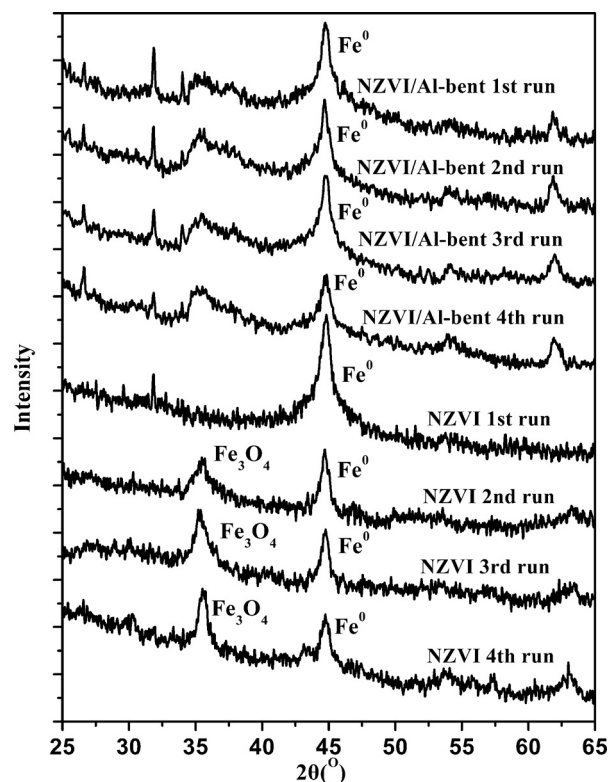


Fig. 5. XRD analysis of NZVI and NZVI/Al-bent after each reaction cycle in the recycling experiments.

microscope (TEM). As shown in Fig. S2, the bare NZVI (Fig. S2A) exists as necklace-like aggregation, while NZVI/Al-bent (Fig. S2B) or NZVI/Na-bent (Fig. S2C) were clearly discrete and well dispersed on the Al-bent or Na-bent carrier.

The higher stability of Al-bent-supported NZVI can be further confirmed by XRD analysis of NZVI and NZVI/Al-bent after each reaction cycle. According to the results shown in Fig. 5, for the NZVI sample, the characteristic peak of Fe_3O_4 at 35.5° appeared obviously after the second run, and further increased after the third run. However, for the NZVI/Al-bent composite, the broad peak at 35.5° did not change as sharply as that observed on the NZVI sample after four cycles, implying fewer oxides formed on the NZVI/Al-bent composite, which may be related to the buffering effect of some particular functional groups in the bentonite as the support [31].

3.3. Buffering effect of the pillared bentonite on medium pH

The effects of pH on Se(VI) removal from water by NZVI and NZVI/Al-bent at the same content of iron are illustrated in Fig. S3A and B, respectively. As we can see from Fig. S3A, the removal efficiencies of Se(VI) by NZVI were 69.9%, 62.1%, 51.8% at pH of 4.0, 6.0, and 8.0, respectively after 120 min. This result indicates that the removal efficiency decreased remarkably with increasing pH. The reaction mechanism of Se(VI) by NZVI appears to be that Fe^0 is oxidized to ferrous ions through anoxic corrosion or reductive dissolution of iron by Se(VI) under anaerobic conditions. At high pH, the formed ferrous ions reacted with generated OH^- , and then oxidized into ferric oxide and hydroxide, which are deposited on the iron surface. When the oxide layer becomes too thick, electron transport through the layer is inhibited, and thus Se(VI) reduction decreased [5]. However, the removal efficiencies of Se(VI) by NZVI/Al-bent were 98.1%, 95.7%, 92.2% at pH of 4.0, 6.0, and 8.0 (Fig. S3B), respectively, namely the removal efficiency slightly decreased as the pH increased from 4.0 to 8.0, which is probably attributed

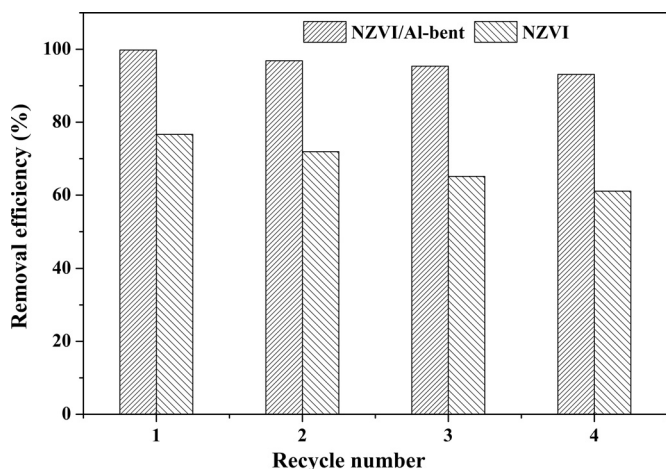


Fig. 4. Results of recycling experiments of Se(VI) removal by NZVI and NZVI/Al-bent.

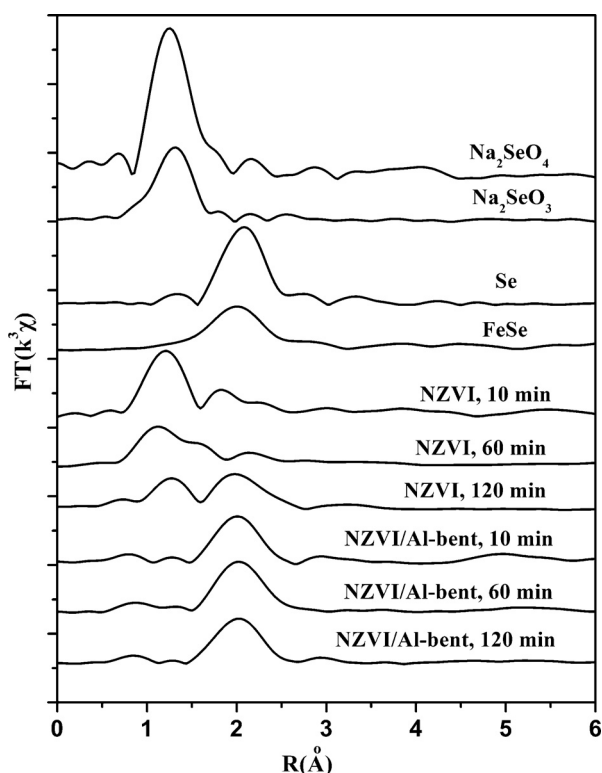


Fig. 6. Extended X-ray absorption fine structure (EXAFS) spectra of four Se reference compounds and two reacted samples with Se(VI).

to the buffering effect of aluminol or silanol groups on Al-bent [34]. Fig. S4 shows the variation of pH during the reaction process of Se(VI) removal by NZVI and NZVI/Al-bent at the same initial pH = 6.0. The pH increased rapidly within 20 min in both systems. Then, the pH value reached close to 8.7 in the NZVI system while maintain at ~7.9 in the NZVI/Al-bent system during the reaction. The result indicates that use of Al-bent as the support of NZVI could maintain a lower pH in the NZVI/Al-bent treatment. As pH increased with H^+ being consumed, the protons could be released into the solution from aluminol or silanol groups of Al-bent [35], compensating the depletion of H^+ . Therefore, less iron oxide layer was formed on the NZVI/Al-bent, and the surface passivation of iron may be reduced. In view of practical application, using Al-bent as the support can expand the pH range for treatment of pollutants with NZVI.

3.4. Transformation of insoluble reduction products away from iron surface by the pillared bentonite

The extended X-ray absorption fine structure (EXAFS) was employed to determine the local atomic structure of Se during the reaction, and the fitting results for the four Se reference compounds and reacted samples of Se(VI) with NZVI or NZVI/Al-bent at different reaction time are shown in Fig. 6 and Table 2. Fitting the Na_2SeO_4 data resulted in a single shell of 4 O atoms at $R_{Se-O} = 1.64 \text{ \AA}$, while the Na_2SeO_3 was fitted with a single shell of 3 O atoms at $R_{Se-O} = 1.70 \text{ \AA}$. For Se(0) sample, the fits lead to three subshells of Se-Fe bond at $R_{Se-Fe} \sim 2.38 \text{ \AA}$ with $N \sim 2.0$, $R_{Se-Fe} \sim 3.53 \text{ \AA}$ with $N \sim 8.0$ and $R_{Se-Fe} \sim 4.04 \text{ \AA}$ with $N \sim 4.0$. While, for FeSe sample, the fits lead to two subshells of Se-Fe bond at $R_{Se-Fe} \sim 2.40 \text{ \AA}$ with $N \sim 4.0$ and $R_{Se-Fe} \sim 4.01 \text{ \AA}$ with $N \sim 8.0$. For the samples of Se(VI) reacted with NZVI, the fits yield a shell of Se-O bond at $R_{Se-O} = 1.64 \text{ \AA}$ with $N = 3.2$ with 10 min, $N = 2.9$ with 60 min, $N = 2.3$ with 150 min, respectively, which agree well with the Se-O distance of Na_2SeO_4 .

Table 2

EXAFS results of reacted samples at Se K-edge

Samples	E_0 (eV)	Shell	$R(\text{\AA})$	N	$\sigma^2(\text{\AA}^2)$
Na_2SeO_4	12666.54	Se-O	1.64	4.0	0.007
Na_2SeO_3	12662.07	Se-O	1.70	3.0	0.005
Se(0)	12658.56	Se-Se	2.38	2.0	0.009
		Se-Se	3.53	8.0	0.021
		Se-Se	4.04	4.0	0.044
FeSe	12657.04	Se-Fe	2.40	4.0	0.015
		Se-Se	4.01	8.0	0.032
NZVI, 10 min	12665.04	Se-O	1.64	3.2	0.009
		Se-Fe	2.39	3.7	0.048
		Se-Se	4.03	7.8	0.055
NZVI, 60 min	12665.49	Se-O	1.64	2.9	0.011
		Se-Fe	2.41	3.5	0.028
		Se-Se	4.05	7.7	0.047
NZVI, 120 min	12657.59	Se-O	1.64	2.3	0.009
		Se-Fe	2.39	3.5	0.021
		Se-Se	4.02	7.9	0.039
NZVI/Al-bent, 10 min	12657.57	Se-Fe	2.39	4.0	0.015
		Se-Se	4.06	8.0	0.034
		Se-Al/Si	3.25	1.3	0.039
NZVI/Al-bent, 60 min	12657.44	Se-Fe	2.39	4.0	0.018
		Se-Se	4.04	8.0	0.026
		Se-Al/Si	3.26	1.7	0.046
NZVI/Al-bent, 120 min	12657.89	Se-Fe	2.40	4.0	0.015
		Se-Se	4.03	8.0	0.024
		Se-Al/Si	3.25	2.3	0.041

This indicates that some of Se(VI) are adsorbed on the surface of NZVI. The decrease of N at long reaction time suggests that the adsorbed Se(VI) could be slowly reduced with reaction proceeding. However, for the samples of Se(VI) reacted with NZVI/Al-bent, the shell of Se-O bond is not obtained, indicating that the absence of adsorbed Se(VI) on the solid, and Se(VI) is completely reduced. In addition, for both samples of Se(VI)-treated NZVI and NZVI/Al-bent, the fits yield two subshells of Se-Fe bond at $R_{Se-Fe} \sim 2.40 \text{ \AA}$ with $N \sim 4.0$ and $R_{Se-Fe} \sim 4.05 \text{ \AA}$ with $N \sim 8.0$. These distances agree well with the Se-Fe distance found for the FeSe sample, indicating that the reduction products of Se(VI)-treated NZVI and NZVI/Al-bent are FeSe. Of particular value is the presence of Se-Al/Si signal ($\sim 2.0 \text{ Al/Si}$ at $\sim 3.25 \text{ \AA}$) in the Se(VI)-treated NZVI/Al-bent sample, suggesting the transfer of some insoluble precipitates away from iron surface by Al-bent, which is an important factor for the enhanced reactivity and stability of NZVI by the introduction of Al-bent as support.

3.5. Activation of Fe(II) ions by the pillared bentonite

In order to further investigate the mechanism of enhanced removal of Se(VI) by NZVI/Al-bent, an experiment was conducted on the reaction of excess Se(VI) (initial 1.5 mmol/L) with NZVI or NZVI/Al-bent containing 2.0 mmol/L iron in the buffer solutions of pH = 6.0 (4-Morpholineethanesulfonic acid hydrate, MES), 7.0 (3-(N-Morpholino) propanesulfonic acid, MOPS) and 8.0 (Tris-(hydroxymethyl) aminomethane, Tris), respectively. The results of particular interest shown in Fig. 7 are observed in the treatment at pH = 8.0 (a pH value comparable to that measured in Fig. S4), it can be calculated that only 0.42 mmol Se(VI) is reduced by NZVI, while 0.6 mmol Se(VI) is removed by NZVI/Al-bent at the same dose of iron. This indicates that the reduction of Se(VI) by per unit mass of iron can be increased by supporting NZVI on Al-bent, which should be related to Fe(II) ions in the composite system. Tang et al. [36,37] found that Fe(II) ions and some other bivalent metal cations (e.g., Co(II)) could dramatically enhanced the Se(VI) removal by ZVI, but Fe(II) ions alone showed insignificantly removal of Se(VI) without the presence of ZVI [36]. In this study of insufficient iron supply, NZVI was almost completely consumed and mostly converted into Fe(II) ions, and Fe(II) ions could reduce only a few of extra Se(VI) [36]. In contrast, the generated Fe(II) ions during the reaction in the

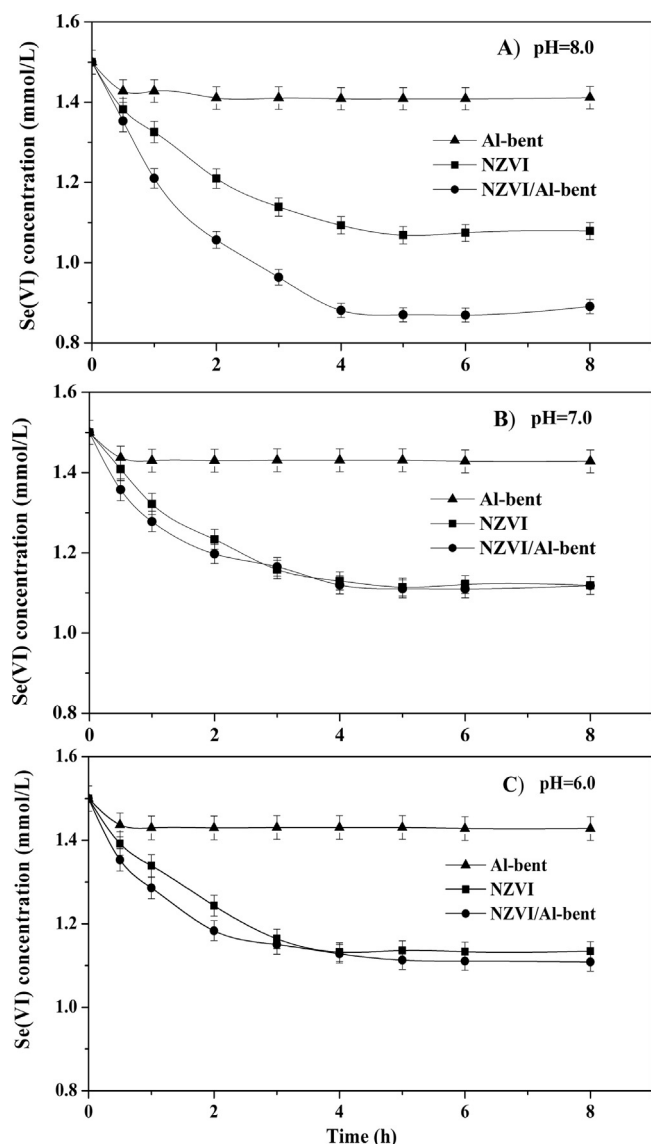


Fig. 7. The results of the reaction of excessive Se(VI) (1.5 mmol/L) with NZVI/Al-bent or NZVI containing 2.0 mmol/L iron at various pH: (A) pH = 8.0, (B) pH = 7.0 and (C) pH = 6.0.

NZVI/Al-bent system will be bound on the bentonite surface. The clay-bound Fe(II) ions had shown their reduction capacity to both metallic and organic pollutants [38,39]. However, the enhanced Se(VI) removal by NZVI/Al-bent was obtained only at pH = 8.0, but neither at pH = 6.0 nor at pH = 7.0. This unexpected result may be explained by the different bonding of Fe(II) ions with bentonite at different pH. Schaefer et al. [40] found that there existed two surface bound Fe(II) species on nontronite (a species of montmorillonite containing iron), i.e., edge OH-group bound Fe(II) and basal plane-adsorbed Fe(II). At pH < 7.5, the main species is basal plane-adsorbed Fe(II) of little reactivity, while at pH > 7.5, the main species is edge OH-group bound Fe(II) of high reactivity. Chakraborty et al. [38] studied the effect of pH on reduction of U(VI) by Fe(II) adsorbed on montmorillonite, and reported that little reduction occurred at pH = 6.1, while ~58% and ~96% of U(VI) was reduced to U(IV) by Fe(II) sorbed on montmorillonite at pH = 7.5 and 8.5, respectively. In this context, we may propose that the adsorption of Fe(II) occurs mainly in the basal plane (low reactive site) of Al-bent at pH < 7.5, and on the edge OH-groups (high reactive site) at pH > 7.5. Consequently, in the buffer solutions of pH = 6.0 and 7.0, Fe(II) ions

adsorbed on the basal plane of Al-bent can hardly reduce Se(VI), whereas, in the pH = 8.0 buffer solution, Fe(II) ions bound on the edge OH-groups of Al-bent are reactive enough to further reduce Se(VI). Thus, the removal of Se(VI) is greatly enhanced. This result is in consistent with the enhanced reduction of U(VI) by per unit mass of iron using bentonite as support in our previous work [31]. This once again proved that, in suitable pH medium, the Fe(II) adsorbed on Al-bent indeed showed high reactivity and increased the reduction capacity of per unit mass of iron.

Combined with results on the removal of contaminants by bentonite-supported NZVIs obtained in this and our previous studies [16,31], we find that the correct matching of bentonite support with target contaminant is essential for the enhanced removal efficiency. That is, the hydrophobic surface of organobentonite, positively charged surface of Al-bent and negatively charged surface of Na-bent favor the adsorption to organic, anionic and cationic contaminants, respectively, and lead to the accelerated reduction of contaminants by NZVI supported on the corresponding bentonite. Other functions of bentonite, such as pH buffering, may also contribute to the synergetic effect of bentonite on reduction of contaminants by NZVI.

4. Conclusions

This study shows that the positively charged surface of Al-bent makes it an excellent candidate as the support of NZVI for removing anionic Se(VI). The synergetic effect of Al-bent relies on its multiple roles as adsorbent of Se(VI), pH buffering agent, carrier for transferring the insoluble reduction products, and finally as the adsorbent of Fe(II) for the enhanced reduction capacity of NZVI. The findings are beneficial for efficient utilization of natural minerals in developing novel techniques for environmental remediation, particularly the in-situ remediation of groundwater with combination of NZVI and an appropriately modified bentonite.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.03.025>.

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